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(19) (CA) **CANADIAN PATENT** (12)

(54) Branched-Chain Amines and Derivatives Thereof

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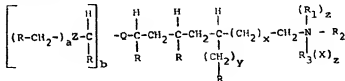
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ABSTRACT OF THE DISCLOSURE

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Novel compounds of the following formula are

disclosed:



wherein x and y are either 0 or 2, provided that x = 0, if

y = 2 and x = 2, if y = 0;

R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>, wherein n represents an integer from 3 to 42;

b is 0 or 1, wherein

if b = 0, Q represents a hydrogen atom, and if b = 1,

Q represents a CH<sub>2</sub>-group;

a = 0 or 1, wherein

if a = 0, Z represents a hydrogen atom, and

if a = 1, Z represents a CH<sub>2</sub>-group;

z is 0 or 1; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> independently represent hydrogen

or an alkyl or alkylene group containing from 1 to about

40 carbon atoms; and X is an anion. A urea obtained by

reacting the above compound with an isocyanate. The compounds

are especially useful as corrosion inhibitors, in mineral

floatation, as fertilizer anticaking agents, as lubricant

additives, fuel additives, mold release agents, fabric

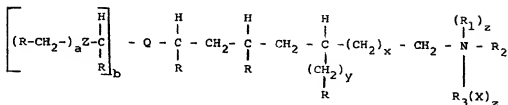
softeners, biocides, demulsification agents, in the prepara-

tion of surface active compounds and in the preparation of

emulsifiers for bitumen.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A compound of the formula



wherein x and y are either 0 or 2, provided that x = 0, if

y = 2 and x = 2, if y = 0;

R = CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>, wherein n represents an integer from 3 to 42;

b is 0 or 1, wherein

if b = 0, Q represents a hydrogen atom, and if b = 1, Q represents a CH<sub>2</sub>-group;

a = 0 or 1, wherein

if a = 0, Z represents a hydrogen atom, and

if a = 1, Z represents a CH<sub>2</sub>-group;

z is 0 or 1; R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> independently represent hydrogen or an alkyl or alkylene group containing from 1 to about 40 carbon atoms; and X is an anion.

2. The compound of claim 1 wherein z is 0.

3. The compound of claim 2 wherein n is about 3 to about 17.

4. The compound of claim 1 wherein z is 1.

5. The compound of claim 4 wherein n is 17 to 42.

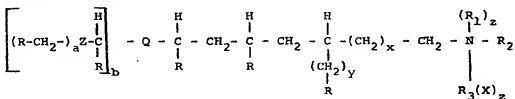
6. The compound of claim 1, wherein R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are selected from the group consisting of alkyl groups having from 1 to 3 carbon atoms, cycloalkyl groups having from 3 to 6 carbon atoms and/or polyalkylene oxide containing groups having from 2 to 30 alkylene oxide units each containing from 2 to 4 carbon atoms.

7. The compound of claim 2, 3 or 4, wherein  $R_1$ ,  $R_2$  and  $R_3$  are selected from the group consisting of alkyl groups having from 1 to 3 carbon atoms, cycloalkyl groups having from 3 to 6 carbon atoms and/or polyalkylene oxide containing groups having from 2 to 30 alkylene oxide units each containing from 2 to 4 carbon atoms.

8. The compound of claim 5, wherein  $R_1$ ,  $R_2$  and  $R_3$  are selected from the group consisting of alkyl groups having from 1 to 3 carbon atoms, cycloalkyl groups having from 3 to 6 carbon atoms, and/or polyalkylene oxide containing groups having from 2 to 30 alkylene oxide units each containing from 2 to 4 carbon atoms.

9. The compound of claim 6 or 8, wherein the alkyl groups are unsubstituted or substituted with one or more lower alkyl or alkoxy groups, halogen atoms, cyano groups, or nitro groups.

10. A urea obtained by reacting an isocyanate with a compound of formula 1



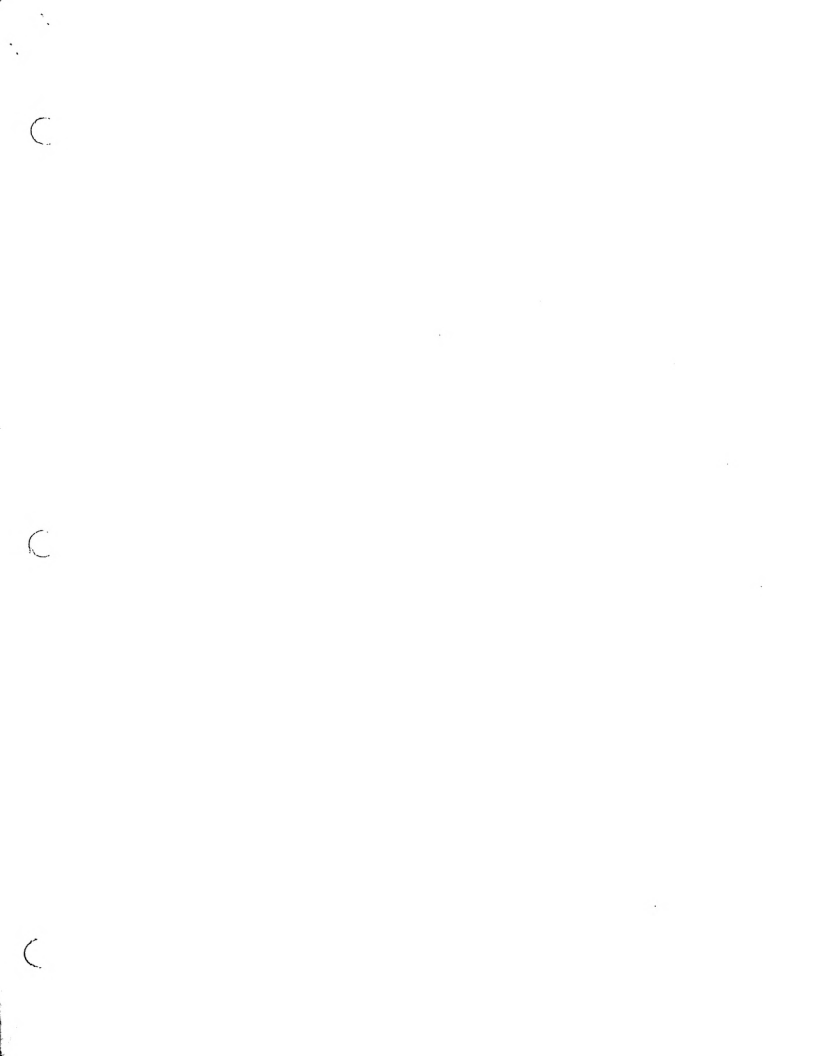
wherein  $x$  and  $y$  are either 0 or 2, provided that  $x = 0$ , if  $y = 2$  and  $x = 2$ , if  $y = 0$ ;

$R = CH_3(CH_2)_n$ , wherein  $n$  represents an integer from 3 to 42;

$b$  is 0 or 1, wherein

if  $b = 0$ ,  $Q$  represents a hydrogen atom, and if  $b = 1$ ,  $Q$  represents a  $CH_2$ -group;

$a = 0$  or 1, wherein



if  $a = 0$ ,  $Z$ ) represents a hydrogen atom, and  
 if  $a = 1$ ,  $Z$ ) represents a  $\text{CH}_2$ -group;  
 $z$  is 0:  $R_1$  represents hydrogen or an alkyl or alkylene group  
 containing from 1 to about 40 carbon atoms;  $R_2$ ,  $R_3$ , or both  
 are hydrogen; and  $X$  is an anion.

11. The urea of claim 10 wherein the isocyanate has  
 the formula  $\text{A-R}_4\text{-NCO}$ , wherein  $R_4$  represents a (cyclo)  
 aliphatic hydrocarbon having from about 6 to about 20 carbon  
 atoms, a phenyl group, a naphthyl group, and  $A$  represents an  
 $\text{-NCO}$  group, or an  $\text{-R}_5\text{-(CH}_2\text{-R}_6\text{-NCO)}_n$   $R_7$  NCO group where  $R_5$  is  
 either a simple bond or an aliphatic hydrocarbon group having  
 1 to 4 carbon atoms,  $n$  is an integer from 0 to 10, and  $R_6$   
 and  $R_7$  may be the same or different and is selected from the  
 same group as  $R_4$ .

12. The urea of claim 10 wherein the isocyanate is  
 selected from the group consisting of ethyl isocyanate, hexyl  
 isocyanate, 2-ethylhexyl isocyanate, butyl isocyanate, stearyl  
 isocyanate, hexamethylene diisocyanate, dimethyl hexamethylene  
 diisocyanate; metaxylene diisocyanate; paraxylene diisocyanate;  
 tetramethylene diisocyanate, 1-chloro-2,4-phenylene  
 diisocyanate, 2,4-toluene diisocyanate, a mixture of 2,4-  
 toluene diisocyanate and 2,6-toluene diisocyanate, tetra-  
 methylphenylene diisocyanate, diphenylmethane-4,4'-diiso-  
 cyanate, metaphenylene diisocyanate, paraphenylene diiso-  
 cyanate, 1,5-naphthalene diisocyanate, biphenyl-4,4'-diiso-  
 cyanate, diphenylmethane-4,4'-diisocyanate, 4,4'-isopropyl-  
 idene diphenylisocyanate, benzophenone-4,4'-diisocyanate,  
 diphenylether diisocyanate, diphenylsulphide diisocyanate,  
 3,3'-dimethyldiphenyl-4,4'-diisocyanate, 3,3'-dimethoxy-

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diphenyl-4,4'-diisocyanate, 3,3'-dichlorodiphenyl-4,4'-diisocyanate, benzofuran-2,7-diisocyanate, isophoron diisocyanate, dicyclohexyl methane diisocyanate and 1,4-cyclohexane diisocyanate.

BACKGROUND OF THE INVENTION

This invention relates to primary mono-amines and derivatives thereof, wherein the mono-amine has a branched-chain.

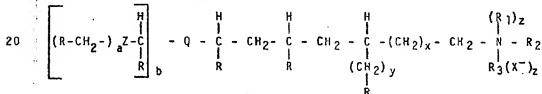
Primary mono-amines and derivatives thereof, such as secondary and tertiary amines, quaternary ammonium compounds, ureas, and salts of organic and inorganic acids are widely known and used in many commercial applications, such as corrosion inhibition, conditioning and water/oil demulsification.

There is a continuing need for new products of the aforementioned type and especially for such products which exhibit additional advantages over the currently available products, as in improved physical or handling properties or better application performance.

An object of the present invention is to provide a new class of branched-chain mono-amines and derivatives thereof.

SUMMARY OF THE INVENTION

Compounds of the following formula have now been provided by the present invention:



wherein x and y are either 0 or 2, provided that x = 0, if y = 2 and x = 2, if y = 0;

25 R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>, wherein n represents an integer from 3 to 42;

b is 0 or 1, wherein

if b = 0, Q represents a hydrogen atom, and if b = 1, Q represents a CH<sub>2</sub>-group;





a = 0 or 1, wherein

if a = 0, Z represents a hydrogen atom, and

if a = 1, Z represents a CH<sub>2</sub>-group;

z is 0 or 1; R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> independently represent hydrogen

or an alkyl or alkylene group containing from 1 to about 40 carbon atoms; and X is an anion.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that for a large number of uses of the compounds of the present invention it is preferred that they conform to the above formula wherein n is from about 3 to about 17. The compounds find application as corrosion inhibitors, in mineral flotation, as fertilizer anticaking agents, as lubricant additives, fuel additives, mold release agents, fabric softeners, biocides, demulsification agents, in the preparation of surface active compounds and in the preparation of emulsifiers for bitumen.

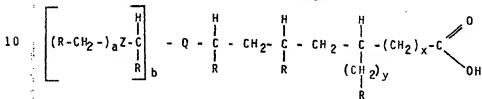
Particularly with a view to the use in fabric softener compositions it is preferred to employ branched-chain amines of the above formula wherein n represents an integer of from 17 to 42. The ureas of the above-formula are used as substitutes for carnauba and/or montan wax.

For many applications the object will be to obtain good processing properties in combination with minimum volatility. According to the invention the secondary, tertiary or quaternary amines are made up then of at least two structural units of the above-formula.

Suitable compounds are obtained when the secondary, tertiary or quaternary amines are made up of 1 to 3 substituted or unsubstituted alkyl groups having up to 22 carbon atoms, cycloalkyl groups having from 3 to 6 carbon atoms and/or polyalkylene oxide-containing groups having from 2 to 30 alkylene oxide units each containing 2 to 4 carbon atoms.

Suitable for use are a great many substituents, such as lower alkyl or alkoxy groups, a halogen atom, a cyano group or a nitro group.

Highly valuable compounds are obtained if use is made of a hydroxyl group or an amino group. The amines of the above-formula can be obtained through reduction in a known manner from the corresponding nitrile. The nitrile is prepared from the corresponding carboxylic acid having the formula:



where R, Z, Q, a, b, x and y have the above indicated meanings.

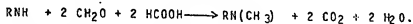
The preparation of nitriles from carboxylic acids is well-known in the art (See e.g., Houben-Weyl, Methoden der organischen Chemie, 4 Ed., Bd. VIII, pp. 335-338).

According to a preferred process the carboxylic acid while in the liquid phase is converted into a mixture of carboxylic acid amide and nitrile, followed by a vapor phase step in which conversion into the nitrile is completed with the aid of a dehydration catalyst.

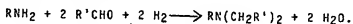
The primary amines are produced by hydrogenation using about 0.5 to 5%, preferably about 1 to about 2%, of a catalyst such as Raney nickel at hydrogen pressures of  $10.10^5$  -  $140.10^5$  Pa and a temperature in the range of  $110^\circ\text{C}$  to  $200^\circ\text{C}$ , or cobalt catalyst at hydrogen pressures of about 600 to about 2,000 psig, preferably about 1,000 to about 1,600, and at a temperature from about  $80^\circ\text{C}$  to about  $200^\circ\text{C}$ , preferably about  $145^\circ\text{C}$ . Increased primary amine formation is favored by the use of alkaline conditions or ammonia plus a lower alcohol. Secondary amine formation is favored by higher temperatures ( $175^\circ$ - $250^\circ\text{C}$ ), exclusion of water, and continuous venting of ammonia. Although both batch and continuous processes may be employed, it is believed preferable to utilize a continuous process.

Tertiary amines built up of one or two structural units according to the invention and two or one lower aliphatic radicals may be prepared by different methods.

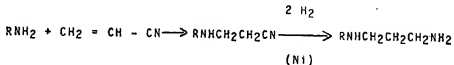
- 5 Methyl groups may be introduced by the reaction between a primary or secondary amine having one or two branched-chain units according to the invention and formic acid and formaldehyde in accordance with the following reaction:



- Mixed tertiary amines may also be prepared by reductive alkylation of a branched-chain primary or secondary amine according to the invention. The amine is subjected to catalytic hydrogenation in the presence of an aldehyde, which may be represented by the following reaction:



- 15 The alkylene oxide derivatives of the present invention are prepared by the bringing a branched-chain primary amine according to the invention into reaction with a lower alkylene oxide such as ethylene or propylene oxide. The amino substituted secondary amines of the invention are prepared from a primary amine having the first-mentioned structural formula and acrylonitrile, followed by catalytic hydrogenation to the diamine:



- The salts of the amines of the present invention may be derived both from organic and inorganic acids. Suitable inorganic acids include phosphoric acid, hydrochloric acid and sulphuric acid. Suitable organic acids are formic acid, acetic acid, propionic acid, butyric acid, stearic acid, oleic acid and rosin acid.

The quaternary ammonium compounds according to the invention may be prepared by introducing up to 3 methyl groups into the formula of claim 1 with the aid of methyl chloride.

- The ureas of the present invention are prepared by reacting a compound of the general formula above wherein  $\overset{Z}{X}$  is and  $R_2$ ,  $R_3$  or both are hydrogen, with an isocyanate. The isocyanates to be used in the preparation of the ureas of the present invention may be of an aliphatic, cycloaliphatic or aromatic character. If few or no colored products are desired, then it is preferred to use aliphatic isocyanates. Preference is further given to isocyanates of the general formula  $A-R_4-\overset{NCO}{HCO}$ , where  $R_4$  represents a (cyclo) aliphatic hydrocarbon having from about 6 to about 20 carbon atoms, a phenyl group or naphthyl group, which groups may be substituted or not with one or more lower alkyl groups having 1 to 8, and preferably 1 to 6 carbon atoms, lower alkoxy groups having 1 to 8, and preferably 1 to 6 carbon atoms, aryl, for instance phenyl, and halogen such as chlorine or bromine, and A represents an  $-NCO$  group, or an  $-R_5-(CH_2-R_6-NCO)_nR_7$   $NCO$  group where  $R_5$  has the meaning of a simple bond or an aliphatic hydrocarbon group having 1 to 4 carbon atoms,  $n$  is an integer from 0 to 10 or higher, and  $R_6$  and  $R_7$  may be the same or different and are selected from the same group as  $R_4$ .

- As examples of suitable monoisocyanates may be mentioned ethyl isocyanate, hexyl isocyanate, 2-ethylhexyl isocyanate, butyl isocyanate, stearyl isocyanate. As examples of diisocyanates which can be defined by the formula  $OCNRRNCO$ , where R represents a divalent aliphatic, cycloaliphatic or aromatic group, may be mentioned:
- hexamethylene diisocyanate;
  - dimethyl hexamethylene diisocyanate;
  - metaxylene diisocyanate;
  - paraxylene diisocyanate;
  - tetramethylene diisocyanate.

In the case where R represents an aromatic group, it may be substituted with a halogen, a lower alkyl or a lower alkoxy group. As examples of such diisocyanates may be mentioned:

- 1-chloro-2,4-phenylene diisocyanate;
- 5 2,4-toluene diisocyanate;
- a mixture of 2,4-toluene diisocyanate and 2,6-toluene diisocyanate;
- tetramethylphenylene diisocyanate;
- diphenylmethane-4,4'-diisocyanate;
- 10 metaphenylene diisocyanate;
- paraphenylene diisocyanate;
- 1,5-naphthalene diisocyanate;
- biphenyl-4,4'-diisocyanate;
- diphenylmethane-4,4'-diisocyanate;
- 15 4,4'-isopropylidene diphenylisocyanate;
- benzophenone-4,4'-diisocyanate;
- diphenylether diisocyanate or diphenylsulphide diisocyanate;
- 3,3'-dimethyldiphenyl-4,4'-diisocyanate;
- 3,3'-dimethoxydiphenyl-4,4'-diisocyanate;
- 20 3,3'-dichlorodiphenyl-4,4'-diisocyanate;
- benzofuran-2,7-diisocyanate.

Examples of diisocyanates having a cycloaliphatic group include isophoron diisocyanate, dicyclohexyl methane diisocyanate and 1,4-cyclo-hexane diisocyanate.

- 25 The temperature at which the reaction takes place between the amine and the isocyanate depends on the reaction components. It will generally be in the range of 10° to 200°C.

- The reaction of the amines according to the invention with the isocyanate compounds is carried out in a known manner.
- 30 The conversion may be carried out in the melt or in an inert solvent. Examples of suitable solvents include methylene chloride, carbon tetrachloride, benzene, chlorobenzene, methylethyl ketone,

tetrahydrofuran, dioxane, glycolmonomethylether acetate, glycol formal, dichlorobenzene, trichlorobenzene, nitrobenzene, benzoic methyl ester or acetophenone. If the conversion is carried out in solvents, especially relatively low boiling ones, such as methylene chloride, the solvents may be distilled off as the reaction progresses.

The starting product required for the preparation of the present amines is obtained by reacting an  $\alpha$ -olefin having 6 to 45 carbon atoms with acetic anhydride at a temperature in the range of 100° to 140°C in the presence of a catalytic amount of an at least trivalent manganese compound. The  $\alpha$ -olefin may consist of a pure olefin fraction, such as 1-octene, or of a mixture of  $\alpha$ -olefins having 6 to 45 carbon atoms. If use is made of a mixture of  $\alpha$ -olefins the number for n in each separate R-radical may, independently of the other R-radicals in the structural formula of the acid and of the amine to be prepared therefrom, assume any value equal to the number of carbon atoms minus two of an  $\alpha$ -olefin present in the mixture.

The most favorable results are generally obtained at a reaction temperature in the range of 115° to 125°C in the presence of manganic acetate as initiator. To prevent oxidation of the substrate the concentration of the manganic acetate is preferably chosen between  $10^{-3}$  and  $10^{-10}$  moles per litre.

The concentration of the olefin fraction is dependent on the desired percentage of branched-chain monocarboxylic acids in the reaction product.

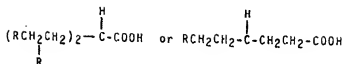
If use is made of an olefin fraction having not more than 12 carbon atoms, preference is usually given to a relatively high percentage of branched-chain acids. If, however, use is made of an olefin fraction having 20 to 45 carbon atoms, then there is found to be a strong preference to a mixture of monocarboxylic

acid which contains at least 70% by weight of the addition product of 1 mole of olefin to 1 mole of acetic acid. In all cases the reaction conditions will be so chosen that ultimately at least 10% by weight of the branched-chain amines conforms to the first-mentioned structural formula. For the preparation of branched-chain monocarboxylic acids from which the amines according to the above formula are derived, the molar ratio of converted olefin to manganic acetate is at least 4. It has been found that under these last-mentioned conditions the composition in weight % of the mixture of telomeric acids and, hence, of the amines prepared therefrom is for  $n \leq 17$  only dependent on the molar ratio of  $\alpha$ -olefin to manganic acetate and the concentration of the  $\alpha$ -olefin during the reaction.

With a monocarboxylic acid obtained, by reacting one  $\alpha$ -olefin with acetic acid, being indicated by  $R_1$ , a monocarboxylic acid obtained by reaction with two  $\alpha$ -olefins by  $R_2$ , a monocarboxylic acid obtained by reaction with three  $\alpha$ -olefins by  $R_3$ , etc., then, for instance, the following weight distribution were obtained respectively before and after removal of the  $R_1$  fraction.

	<u>before distillation</u>	<u>after distillation</u>
	<u>wt %</u>	<u>wt %</u>
$R_1$	30.7	0.3
$R_2$	20.4	19.8
$R_3$	21.4	33.6
$R_4$	13.0	21.5
$R_5$	9.4	15.9
$R_{>6}$	5.1	8.8

The structural formulae of  $R_3$ ,  $R_4$  and  $R_5$  all conform to the first-mentioned formula.  $R_1$  is an unbranched acid of the formula  $R(CH_2)_3 COOH$  and, if  $n = 3$  to 9, it is preferably removed from the reaction mixture. The fraction of  $R_2$  is formed by two acids of the formula:



For a man skilled in the art it is obvious that,  
 5 especially if use is made of an olefin fraction having 30 or more carbon atoms, it is not possible in actual practice to separate the linear acids from the acids having a very high molecular weight and a high degree of telomerization. The same applies to the nitrile and amine derivatives.

10 The following is a typical example of a weight distribution of the monocarboxylic acids obtained under said conditions and, hence, of the amines prepared therefrom.

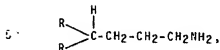
	<u>degree of telomerization</u>	<u>wt %</u>
	m = 1	78.0
15	m = 2	6.3
	m = 3	6.5
	m = 4	4.0
	m = 5	3.1
20	m > 6	2.0

It has been found that as far as the above-mentioned field of application of corrosion inhibitors, surface active compounds etc., is concerned, the use of mixtures of amines derived from those branched-chain and straight-chain carboxylic acids lead to  
 25 compositions having unexpectedly favorable properties, which remarkably favorably compare with the known compositions, which only contain straight-chain amines or the derivatives thereof.

The commercially available olefin fractions having 20 to 45 carbon atoms are found to contain 60 to 80% by weight of  $\alpha$ -olefins  
 30 and for the rest predominantly consist of vinylidene compounds.



The resulting amines are  $\gamma$ -branched monoamines, with the amine having the formula:



where  $R_1$  and  $R_2$  represent linear alkyl groups which together have the same number of carbon atoms as the group  $R$ .

Separation of these vinylidene groups-containing fractions from the  $\alpha$ -olefins would give rise to so many technological problems that it must be considered impracticable for economic reasons.

It has been found, however, that for most uses products having exceptionally good properties are obtained if besides the branched-chain amines having the above formulae or the derivatives thereof there is present an amount of 40 to 60 per cent by weight of the amine fraction or of the derivatives thereof which consists of or is derived from linear aliphatic monoamines, with the amine having the formula  $R\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ , where  $R$  represents a  $\text{CH}_3(\text{CH}_2)_n$  group, with  $n$  being an integer of from 17 to 42.

The invention is further described in, but not limited by the following examples.

#### Example I

A slurry made up of 38 pounds of manganese (III) acetate in 160 pounds of acetic anhydride and was slowly added, with stirring, over a period of about 6 to 14 hours in an atmosphere of dry nitrogen, to a previously provided mixture of 459 pounds (4.5 pound-moles) of acetic anhydride and 60 pounds (1.9 pound-moles) of 1-octene. The reaction temperature was 120°C. When the manganese acetate addition was complete, the reaction mixture was cooled and filtered; the reaction product and the filter cake were washed with hexane and the combined liquid phase recharged to the reactor for vacuum stripping. Hydrolysis of the resultant anhydride was accomplished with water/acetic acid, which was finally stripped off under vacuum.

The residual oil contained 38% capric acid, 2% volatiles, and the remainder was telomeric acid.

Fractional vacuum distillation resulted in obtaining three fractions having the chain-length distributions (given as wt. % according to a GPC analysis) shown in Table I:

TABLE I

weight %		Fraction		
n		A	B	C
1	0.1	0.3	0.7	
2	1.3	1.0	5.0	
3	84.9	12.1	2.4	
4	3.9	61.9	39.5	
5	8.3	20.0	40.6	
6	1.4	4.7	11.8	

x n = degree of telomerization

The telomeric acid fractions were converted into nitrile batch-wise by bubbling ammonia gas through the hot (325°C) acid containing 0.5% catalytic alumina and separating the evolved water via a Dean-Stark trap. The reaction was continued until the conversion to nitrile was approximately 92% (15 to 20 hours). The nitrile was vacuum distilled (yield 85%) and subsequently hydrogenated.

The hydrogenation to primary amine was carried out in a 2.8cm x 45.7cm continuous column containing a cobalt catalyst in the form of 1/8 inch extrudates.

Hydrogenation was performed downflow at 120°C (fraction C) and 145°C (fractions A and B), a pressure of  $70 \times 10^5$  Pa, and a space velocity of 0.7 ml of nitrile 1 hr/ml of bed space.

The molar ratios of  $H_2/NH_3$ /nitrile were 21:27:1 (fractions A and B) and 15:30:1 (fraction C). Of the resulting mixture of amines the chemical analysis and the pour point (in conformity with ASTM D97-66 were determined and are shown in Table II.

The weight percentages of primary, secondary, and tertiary amine shown in Table II are based upon the NE values of the parent acids (A=330, B=620, C=1170) and the weight percentages have not been normalized.

TABLE II

amine \ weight %	Fraction		
	A	B	C
PA	94	106	71
SA	10	3	9
TA	3	13	9
Pour Point	- 50	- 39	+ 8

PA = primary amine, SA = secondary amine, and TA = tertiary amine.

### Example II

In this example dialkyl secondary amines were prepared from the primary amines of the preceding example under the following hydrogenation conditions:

temperature 230°-235°C  
 hydrogen pressure 3.5 x 10<sup>5</sup> PA (with vent)  
 powdered Ni-catalyst 0.5 % by weight

The reaction time varied from 7 hours (fractions A and B) to 20 hours (fraction C).

Of the resulting products the chemical analysis and the pour point are given in Table III.

TABLE III

amine \ weight %	Fraction		
	A	B	C
PA	3	6	8
SA	93	93	89
TA	4	1	8
Pour Point	-50	-43	-25

Example III

Fractions A, B, and C of Example I were cyanoethylated using 10% methanol (based on primary amine) as catalyst at approximately 78°C (reflux). Acrylonitrile was added over thirty minutes and the mixture was refluxed for 2.5 hours. The volatiles were removed in vacuo, and the cyanoamine was reduced to the corresponding diamine under the following reaction conditions:

powdered cobalt catalyst 0.6 % by weight (based on primary amine)

temperature 130°C

partial pressure 28.105 Pa NH<sub>3</sub>

28.105 Pa H<sub>2</sub>

The reaction time was 6-12 hours.

The results are given in Table IV:

TABLE IV				
amine	equivalent ratio	Fraction		
		A	B	C
PA		53	55	62
SA		47	45	38
Pour Point		-45	-32	-12

Example IV

Fractions A, B and C of Example I were ethoxylated to two- and ten-mole ethoxylates under standard conditions.

Two equivalents of ethylene oxide were added from a tared bomb to the amine (N<sub>2</sub> purged) at 170°C and 3.5 x 10<sup>5</sup> Pa. After two hours, the reaction products were cooled and sampled. The ten-mole ethoxylate was prepared from the two mole adduct at 180°C using 1.3% of a 50% aqueous caustic soda solution. The results for the two-mole ethoxylate are shown in Table V. The ten-mole ethoxylate had a pour point of -20°C for fraction A, -14°C for fraction B, and -10°C for fraction C.

TABLE V

weight % amount	Fraction		
	A	B	C
PA	1		
SA	3	5	
TA	96	94	100
Pour Point°C	-28	-22	-17

Example V

10 Fractions A, B and C of Example I were quaternized with methyl chloride at a pressure of  $5.6 \cdot 10^5$  Pa and a temperature of  $80^\circ\text{C}$ , using 2-propanol as the solvent.

Sodium bicarbonate was used to neutralize the two equivalents of HC liberated by the reaction. The reaction vessel was vented periodically to remove carbon dioxide and repressurized with methyl chloride. The reaction times varied from 4 to 8 hours.

Example VI

20 In this Example it will be shown that the branched-chain telomeric amines of the present invention are suitable to be used in bitumen adhesion.

The test procedure was as follows:

1 g of the amine was added to 100 g cut-back bitumen and thoroughly stirred to insure proper dispersion.

25 A metal container (approximately 12.7 cm in diameter) was covered with 15-20 g of said bitumen to a film thickness of about 1.5 mm.

After cooling to  $20^\circ\text{C}$  the container was immersed in water to a depth of about 2.54 cm. Into the bitumen film there were then lightly pressed 10 pieces of granite aggregate having a diameter of about 1.3 cm.

The aggregate was then removed from the binder and the percentage of binder retained on the stone was visually assessed. Both fraction A of Example I and fractions A and B of Example III resulted in 100% coverage.

5 Example VII

In this Example it is shown that the branched-chain telomeric amines of the present invention are suitable to be incorporated into acid pickling inhibitor formulations.

The test consists in storing weighed mild steel coupons in inhibited acid for 3 hours at 90°C and subsequently determining the loss in weight. The test procedure was as follows:

The steel coupons were first degreased in boiling carbon tetrachloride for 5-10 minutes and subsequently in boiling acetone for another 5-10 minutes. Subsequently, they were allowed to cool in a desiccator and weighed.

The coupon was then transferred to a bottle containing 200 ml of a hydrochloric acid pickling solution. The hydrochloric acid (15% w/v) contained a 1% solution of the test material. The temperature of the solution was then kept at 90°C for 3 hours, after which the coupons were removed from the acid, washed thoroughly with water and placed in boiling acetone for 5-10 minutes. After cooling they were re-weighed and the loss in weight was calculated.

The results mentioned in the following table clearly show the superiority of the presently claimed amines to the commercially available straight-chain ones.

	<u>Product</u>	<u>Weight loss % by weight</u>
30	Commercial corrosion inhibitor containing a straight-chain amine	0.25
	Same formulation based on an amine of	
	Example I A	0.13
	Example I C	0.20
35	Example III A	0.23
	Example III B	0.17

Example VIII

The same procedure was used as in Example VII, except that the test was carried out now in sulphuric acid (10% by weight). The concentration of the inhibitor formulation was in this case 0.05% by weight.

The loss in weight of the formulation based on a commercial straight-chain amine was 0.40% by weight, whereas the loss in weight of the same formulation based on the amine of Example IV A was as low as 0.33 % by weight.

10 Example IX

This Example shows the step-wise preparation of a quaternary ammonium compound based on telomeric acid derived from hexene-1.

A. Preparation of Nitrile

15 650 g of a telomeric acid, derived from hexene-1, having an acid value of 160, a saponification value of 194 and a composition of:

1.6%	m = 1
16%	m = 2
29%	m = 3
20%	m = 4
12%	m = 5
17%	m > 6

and 3.5 g of cobalt (II) oxide were heated in a stainless steel autoclave at 325°C. Dry ammonia gas was continuously fed to the reactor. A pressure of 6 to 8 bar gauge was maintained by careful venting, removing at the same time the reaction water. After 7.5 hours the reaction was stopped. 79.8 g aqueous phase was collected from the vent line together with 36.2 g fatty acid material. 528 g reaction product remained in the autoclave. The reaction product was distilled at a pressure of 40.0 Pa (0.3 Torr) and a top temperature of 170°C, yielding 76.3% w/w distillate and 22.9% w/w residue. The distillate contained 92.1 % w/w nitrile, 1.2% w/w telomeric acid and 6.7% w/w apparent soap and amide.

B. Preparation of Primary Amine

120 g of this distillate, being the telomeric nitrile, derived from hexene-1, was heated in a Hastelloy "C" autoclave together with 5.4 g B133 Co-catalyst (Degussa) and 12 g ammonia for 5 hours at 180°-200°C. The autoclave was pressurized with hydrogen to 100 bar gauge. The filtered reaction product contained 74.6% w/w primary amine, 13.1% w/w secondary amine and 12.3% w/w tertiary. Hastelloy is a trademark of Union Carbide Corporation, 270 Park Avenue, New York, N.Y. 10017, for a series of high strength nickel base, corrosion resistant alloys. They are commonly used in reactors because of their inert nature.

C. Preparation of Quaternary Ammonium Compound

96.2 g of the mixture of amines was heated in a glass autoclave together with 300 g isopropanol, 124.6 g sodium carbonate decahydrate and 109.1 g methyl chloride at 100°C for 5.5 hours, exerting a pressure of 6 bar absolute. At the end of the reaction, the inorganic salt was filtered off and the isopropanol and water were evaporated at 2.7 kPa (20 Torr) and 70°C, yielding 112.2 g reaction product. Analysis of the product revealed that the quaternary ammonium chloride content was 1.86 meq/g, corresponding with approx. 94% w/w. From the composition of the starting amine, it can be calculated that this consists of 73% w/w monotelomeric trimethyl ammonium chloride, 11% ditelomeric dimethyl ammonium chloride and 10% tritelomeric methyl ammonium chloride.

Other analytical data: 0.8% w/w water, 0.1% w/w free amine, 0.1% w/w amine hydrochloric acid salt.

The product appeared to be a liquid at room temperature. This liquidity in solvent-free form is a remarkable advantage over e.g. stearyl trimethyl ammonium chloride which melts only over 200°C and must be diluted with alcohol/water



to get lower melting points.

Example X

This Example shows the step-wise preparation of quaternary ammonium compound based on telomeric acid derived from octene-1.  
5

A. Preparation of Nitrile

682 g of telomeric acid, derived from octene-1, having an acid value of 168, a saponification value of 187 and a composition of:

< 1%	m = 1
87%	m = 2
11%	m = 3
< 1%	m = 4

- 5 and 4.4 g cobalt (II) oxide were heated in a stainless steel autoclave at 325°C. Dry ammonia gas was continuously fed to the reactor. A pressure of 6 to 8 bar gauge was maintained by careful venting, removing at the same time the reaction water. After 12 hours the reaction was stopped. 95 g aqueous phase was collected
- 10 from the vent line together with 28.5 g fatty acid material.. 566.1 g reaction product remained in the autoclave, containing about 1% w/w telomeric acid and 4.8% w/w apparent soap and amide. The reaction product was distilled at a pressure of 160 Pa (1.2 Torr) and a top temperature of 170°C, yielding 84% w/w distillate
- 15 and 14.4 w/w residue. The distillate contained 94.9% w/w nitrile, 0.2% w/w telomeric acid and 4.8% w/w apparent soap and amide.

#### B. Preparation of Secondary Amine

- 120 g of this distillate, being the telomeric nitrile, derived from octene-1, was heated in a Hastelloy "C" autoclave together
- 20 with 3.2 g Co-catalyst for 2.5 hours at 180°C (step 1) and for 2.5 hours at 220°C (step 2). During step 1 the autoclave was pressurized with hydrogen to 50 bar gauge. During both step 1 and 2 the autoclave was periodically vented and flushed with hydrogen. 115.7 g of filtered reaction product was obtained, containing 3.6%
- 25 w/w primary amine, 87.6 w/w secondary amine and 8.9% w/w tertiary amine.

#### C. Preparation of Quaternary Ammonium Compound

- 102.4 g of this mixture of amines was heated in a glass autoclave together with 300 g isopropanol, 53.6 g sodium carbonate
- 30 decahydrate and 47.6 g methyl chloride at 100°C for 6 hours, exerting a pressure of 6 bar absolute. At the end of the reaction the salts were filtered off and the isopropanol and water were distilled off at 2.7 kPa (20 Torr) and 70°C, yielding 111.4 g reaction product.

Analysis of the product revealed that the quaternary ammonium chloride content was 1.51 meq/g, corresponding with approximately 92% w/w. From the composition of the starting amine it can be calculated that this consists of 4% w/w monotelomeric trimethyl ammonium chloride, 80% w/w ditelomeric dimethyl ammonium chloride and 8% w/w tritelomeric methyl ammonium chloride.

Other analytical data: 0.1% w/w free amine, 0.2% w/w amine hydrochloric acid salt and 0.1% water.

The product appeared to be liquid at room temperature. This liquidity is a remarkable advantage over distearyl dimethyl ammonium chloride, which melts at 115°C in pure form and at approximately 40°C when diluted with 25 % isopropanol/water.

#### Example XI

This Example demonstrates the ability of the two quaternary ammonium compounds from Examples IX and X to demulsify oil-in-water emulsions. The quaternary ammonium compounds of the Examples are compared to a commercially available quaternary ammonium compound dimethyl dicocoammonium chloride as sold by Armak Company, Chicago, Illinois, under the trademark Arquad®2C-75 and to a nonionic surfactant of the structure  $\text{HO}(\text{EO})_a(\text{PO})_b(\text{EO})_c\text{H}$ , wherein EO represents ethylene oxide linkages and PO represents propylene oxide linkages, sold under the trademark Dissolvlan 4460 by Hoechst.

Standary emulsions were prepared by mixing equal amounts (50ml oil/50ml water) of oil from the forties field in the North Sea and water in an Ultra Turrax mixer for 20 minutes at maximum speed. The temperature of the emulsions during mixing was maintained at a maximum of 40°C through ice cooling.

Immediately after the emulsions were prepared, they were conditioned at 40°C and 60°C in 100 ml calibrated glass cylinders. Subsequently, the demulsifier to be tested was added in

isopropanol at concentrations of 10, 25, 50 and 100ppm, and the mixture homogenized by shaking manually. The amount of water removed was measured as a function of time and the demulsifications were preformed at both 40°C and 60°C. The results of the demulsifications are shown in the following Tables VI and VII and demonstrate that the quaternary ammonium compound of Examples IX and X both demulsify the oil/water emulsion with the compound of Example IX being more effective than the compound of Example X, but less effective than the commercially available demulsifier Dissolvan 460. The corresponding dimethyldicocoammonium chloride did not act as demulsifier.

Table VI. Demulsification of Forties emulsions (50 ml oil, 50 ml water) T = 40°C. Figures denote ml. of water separated.

	Demulsifier/Conc.ppm	10min. 20min. 30min. 1h 2h 3h 4h 5h 24h									
15	Example IX/10 ppm							1	30		
	Example IX/25 ppm					2		43	45		
	Example IX/50 ppm			39	45	48	48	49	49		
	Example IX/100 ppm	43	44	45	48	49	49	49	49		
20	Example X/10 ppm							1	1		
	Example X/25 ppm							21	36		
	Example X/50 ppm			1	4	27	42	42	45		
	Example X/100 ppm	14	47	49	49	49	49	49	49		
25	Dissolvan 4460/10 ppm					4				48	
	Dissolvan 4460/50 ppm	43	46	48	48						
	Dissolvan 4460/100 ppm	49									
	Arquad <sup>®</sup> 2 HT-75/10 ppm										

Table 2. Demulsification of Forties emulsions (50 ml oil, 50 ml water)  $T = 60^{\circ}\text{C}$ . Figures denote ml. of water separated.

<u>Demulsifier/Conc.ppm</u>		<u>2min.</u>	<u>8min.</u>	<u>15min.</u>	<u>30min.</u>	<u>1h</u>	<u>2h</u>	<u>4h</u>	<u>4h</u>
5	22 TL 2073/10 ppm				5	33	48	50	
	22 TL 2073/25 ppm			5	43	49	50		
	22 TL 2073/50 ppm		44	46	47	50			
	22 TL 2073/100 ppm	22	46	48	49				
	23 TL 2073/10 ppm					8	44	47	49
10	23 TL 2073/25 ppm				24	44	50		
	23 TL 2073/50 ppm		1	3	42	50			
	23 TL 2073/100 ppm	1	32	50					

#### EXAMPLE XII

This example shows the step-wise preparation of a diamine based on telomeric acid derived from 1-decene.

#### 15 A. Preparation of Nitrile

A telomer acid derived from 1-decene, acetic anhydride, and manganese II acetate utilizing a process similar to Example I, having a neutralization equivalent of 514 was converted to nitrile batch-wise by bubbling ammonia gas through hot ( $325^{\circ}\text{C}$ ) acid  
20 containing 0.5% catalytic alumina and separating the evolved water via a Dean-Stark trap. After 10 hours the conversion to nitrile was approximately 93%.

#### B. Preparation of Monoamine

This nitrile from A above, without separation, was reduced  
25 utilizing a continuous downflow process employing a cobalt catalyst. The reaction temperature was  $140^{\circ}\text{C}$ , the pressure was  $70 \times 10^5$  Pa, the space velocity was 0.7, and the molar ratio of  $\text{H}_2/\text{NH}_3/\text{nitrile}$  was 12:17:1. The resulting amine was analyzed as being 80% primary amine, 7% secondary amine, 5% tertiary amine  
30 (based on theoretical molecular weight from acid).

C. Preparation of Diamine

The amine from B above was cyanoethylated using 8% methanol catalyst (based on amine). Acrylonitrile was added over 25 minutes and the mixture was refluxed for 9 hours. The volatiles were removed in vacuo, and the cyanoamine was reduced to the corresponding diamine under the following condition:

catalyst (Raney Nickel)	1% by weight
temperature	130°C
pressure	28x10 <sup>5</sup> Pa NH <sub>3</sub>
10	28x10 <sub>5</sub> Pa H <sub>2</sub>

The reduction time was 4 hours and the resultant diamine content was 70%.

**SUBSTITUTE**  
***REPLACEMENT***

**SECTION is not Present**  
***Cette Section est Absente***